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54 **Method for concentrating solutions by means of reverse osmosis.**

57 The invention relates to a method and apparatus for concentrating solutions by means of reverse osmosis on the basis of a combination of membrane modules (A) having membranes with high retention, and membrane modules (B) having membranes with limited retention, the minimum number of membrane modules being three. Any membrane module may be replaced by a continuous membrane column. At least one of the membrane modules (A) and (B) should be in the form of a cascade, comprising preferably from two up to and including eight membrane modules.

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Method for concentrating solutions by means of reverse osmosis.

The invention relates to a method for concentrating solutions by means of reverse osmosis.

While concentrating solutions by means of reverse osmosis  
5 a limit value for concentrating is reached at increasing concentration of the dissolved material, because the osmotic pressure of the solution increases to such a level, that it approaches the applied pressure. Prior to reaching this point, the transportation gets so low, that it is  
10 no longer acceptable for practical purposes. The selective transportation of solvent through the membrane is the cause that the concentration of the dissolved material at the membrane surface is higher than in the remaining body of the solution. This concentration-polarisation can be reduced  
15 by intensive stirring at the pressure side of the membrane surface, for example with a circulation pump. However the osmotic pressure of a solution remains the limiting factor when concentrating by means of a membrane for reverse osmosis. It will be understood that the applied pressure can not  
20 be increased unlimited, with a view to the limitations imposed by the strength of the material of the membrane and the supporting layers therefore. Though according to theoretical considerations it is desirable to make the difference in concentration over the membrane small, for  
25 example by allowing a certain concentration of the material to be concentrated in solution at the permeate side, in practice this appears to provide unsurmountable problems, in particular as it is not possible to stir at the permeate side because of the supporting layers present there. This  
30 keeps the production limited as well.

The disadvantage of the counteracting osmotic pressure can be mitigated somewhat by using a membrane with a limited retaining capacity  $R$  (retention), such as described in

British Patent Specification No. 1,324,031. The latter method shows a substantial effect with respect to the osmotic pressure only when higher permeate concentrations are allowed.

- 5       The feed concentration should not be lower than the permeate concentration, from a viewpoint of process efficiency, as otherwise a concentration previously obtained will in part be nullified.
- 10   The method according to British Patent Specification No. 1,324,031 thus comprises that the permeate flow of the membrane with limited retention should have a concentration amounting to  $(1 - R) \times$  the concentration of the concentrate. Concentrating by a factor of for example 10 implies that
- 15   the retention of the membrane should amount to 0.9; this will provide only a small advantage with respect to the osmotic pressure.

The invention provides a method and apparatus by which the

20   above disadvantages can be mitigated or even avoided.

More in particular the invention relates to a method for concentrating solutions by means of reverse osmosis, wherein at least one membrane module (A) with a high retention for

25   the compound to be concentrated, is coupled with at least one membrane module (B) with a limited retention for the compound to be concentrated, the permeate from the (last) membrane module (B) being returned towards the (first) membrane module (A), the solvent at the permeate side of the

30   (first) membrane module (A) being removed and the concentrate of the compound to be concentrated being removed at the pressure side of the (first) membrane module (B), while the pressure sides of the (last) membrane module (A) and the (last) membrane module (B) are interconnected, and

35   fresh solution to be treated is supplied at a point in the connection between the permeate side of the (last) membrane module (B) and the pressure side of the (first) membrane

module (A), the total number of membrane modules being at least three.

In a membrane module (B) a membrane with a moderate retention for the compound to be concentrated is used, for example a membrane with a separation factor in the range of  $1 < \alpha < 4$ , wherein

$$\alpha = \frac{1 - x_p}{x_p} \cdot \frac{x_r}{1 - x_r},$$

wherein  $x_p$  is the molar fraction of the dissolved compound in the permeate and  $x_r$  is the molar fraction of the dissolved compound at the high pressure side of the membrane. In this description such membranes will further be referred to as  $\alpha$ -membranes. It has now been found to be possible to obtain a continuous process by a suitable combination of at least one membrane with a high separation factor (herein further referred to as RO-membrane) with at least one  $\alpha$ -membrane, wherein at least two membranes of at least one of the two types should be present, the properties of the two types of membranes being used to obtain on the one hand substantially pure solvent and on the other hand a concentrated solution as product stream, as will be elucidated in more detail hereinbelow.

For obtaining an optimal result it is of importance that the fresh solution to be treated is supplied at a point upstream of a pump positioned in a connection between the permeate side of the (last) membrane module (B) and the pressure side of the (first) membrane module (A). By a suitable selection of the number of modules (A) and (B) in relation to the  $\alpha$ -membrane, on coupling of the modules (A) and (B) a concentration can be obtained which is substantially equal to that of the feed-solution to be treated. Depending on the type of the dissolved compound, the solvent used and the retention of the  $\alpha$ -membrane, it may be advantageous to use instead of one membrane module (B) a cascade of such modules, the arrangement of such a cas-

cade can be one of the many options known for cascades, the selection of the arrangement being governed by the factors mentioned above as well as the yield envisaged. Cascades of two to eight membrane modules (B) are usually  
5 sufficient for the target envisaged, and a necessity when only one membrane module (A) is used. In most cases two to four membrane modules (B) will lead to the target envisaged. If desired one or more membrane modules (B) can be replaced by a continuous membrane column, such as the one  
10 described for gas separations in A.I.Ch.E. Journal, 26, 558 - 566. A continuous membrane column in this context is considered to be equivalent to a plurality of membrane modules.

15 With respect to the membrane modules (A) the same considerations apply as discussed hereinabove with respect to membrane modules (B), implying that there can be a cascade of two to eight of such membrane modules (A), one or more of which may have been replaced by a continuous mem-  
20 brane column as mentioned above. Again such a cascade is a necessity when only one membrane module (B) is used. The use of a cascade or a continuous membrane column provides the additional advantage that a favourable concentration gradient is present along the membrane, making the drop  
25 in concentration over the membrane smaller on average.

When using such a cascade or such a continuous membrane column, the separation factor in the direction of the product flow decreases, preferably from about 4 to 1.1,  
30 while in praxis a somewhat higher/lower limit than 1.1 is usually maintained, as at this latter value the separating potential is particularly small.

The membranes used in the osmosis have usually been made  
35 from the materials customary for that purpose, such as for example cellulose acetate, polysulphones or polyamides. Membranes with a limited retention are obtained by

moderate curing.

In the manner described above it is possible to avoid the limitations of RO-membranes, caused by the osmotic pressure, either completely or at least partially. It has also appeared that the production of concentrate per  $m^2$ /hour may be up to 80% higher under favourable conditions than can be obtained with an RO-cell in the range where the osmotic pressure not yet prevents further concentration with an RO-cell.

Determinative for the retention properties of a membrane is the after-treatment. That may comprise for example a temperature-treatment, a pressure-treatment, solvent shrinkage. Of importance is in that context that the retention properties are homogeneously divided over the surface of the membrane and are not caused or affected by local leakages. It is also possible to manufacture asymmetric membranes, wherein the retention properties of the membrane may be modified in the desired way by changes in the composition of the moulding syrup. By using membranes each having a different separation factor in a cascade, a supplemental possibility is created for highly concentrating solutions.

25

The invention also relates to an apparatus for concentrating a solution by means of reverse osmosis, comprising at least one membrane module (A) with a high retention for the compound to be concentrated, coupled with at least one membrane module (B) with limited retention for the compound to be concentrated, the total number of membrane modules being at least three, wherein the permeate side of the (last) membrane module (B) by means of a conduit is connected to the pressure side of the (first) membrane module (A), and the pressure side of the (last) membrane module (A) by means of a conduit is connected to the pressure side of the (last) membrane module (B), the (first)

membrane module (A) at the permeate side being provided with a conduit for withdrawing solvent, the (first) membrane module (B) being provided with a conduit for withdrawing formed concentrate at the pressure side, a pump 5 being present in the conduit between the (last) membrane module (B) and the (first) membrane module (A) and at a point between this (last) membrane module (B) and the pump a supply conduit for fresh solution to be treated emerges into the connecting conduit.

10

In a preferred embodiment the apparatus of the invention may comprise a cascade of membrane modules (B), more in particular two to eight, while the apparatus if desired may contain a cascade of membrane modules (A), more in 15 particular two to eight. It is also favourable to replace at least one membrane module (A) and/or at least one membrane module (B) by a continuous membrane column. If the apparatus comprises a cascade of membrane modules or a continuous membrane column, these are preferably selected 20 in such a way that the separation factor of the membranes used, or along the continuous membrane column in the direction of the product flow, decreases from 4 to 1.1.

The method and apparatus according to the invention will 25 be elucidated hereinafter with reference to the accompanying drawing, which is a schematic flow diagram of a presently preferred apparatus for concentrating solutions by means of reverse osmosis, comprising a cascade of membrane modules (B), coupled with a cascade of membrane modules (A). 30

The drawing shows a cascade coupling, wherein a first membrane module (B) (21), provided with a membrane (22) with a limited retention, is provided at the pressure 35 side with an outlet conduit (23) for concentrate, while at the permeate side an outlet conduit (24) runs towards the permeate side of a second membrane module (B) (25),

provided with a membrane (26) with limited retention, provided at the pressure side with a connecting conduit (27) to the pressure side of the first membrane module (B) (21) and at the permeate side provided with a connecting conduit 5 (28) to a third (and in this case last) membrane module (B) (29), provided with a membrane (30) with limited retention, provided at the pressure side with a connecting conduit (31) to the pressure side of the second membrane module (B) (25) and at the permeate side provided with a connecting conduit 10 (32), which via a pump (33) and conduit (34) leads towards the pressure side of a first membrane module (A) (35), provided with a membrane (36) with high retention, provided at the permeate side with an outlet conduit (37) for solvent, and at the pressure side provided with a connecting conduit 15 (38) to the pressure side of a second membrane module (A) (39), provided with a membrane (40) with high retention, at the permeate side provided with a connecting conduit (41) to the permeate side of membrane module (A) (35) and at the pressure side provided with another connecting conduit (42) 20 to the pressure side of a third (and in this case last) membrane module (A) (43), provided with a membrane (44) with high retention, provided at the pressure side with a connecting conduit (45) to the pressure side of the last membrane module (B) (29), and at the permeate side provided with a 25 connecting conduit (46) to the permeate side of the second membrane module (A) (39). Into outlet conduit (32) also emerges a supply conduit (47) for fresh solution to be treated.

In a modification of the apparatus as shown in the drawing 30 comprising a cascade of two membrane modules (B) in combination with one membrane module (A) a 2% saccharose solution in water was concentrated to 18% at various reflux ratios under otherwise identical conditions, i.e. membrane modules (B) each had a separation factor of  $\alpha = 2$  and membrane 35 module (A) had a separation factor of  $\alpha > 100$ ; the permeability of the RO-membrane was  $0.003 \text{ g/min.cm}^2\text{.bar}$ ; the permeability of the  $\alpha$ -membrane was  $0.15 \text{ g/min.cm}^2\text{.bar}$ ; the re-



flux ratio is the reflux flow from membrane module (B) to membrane module (A), divided by the product flow. The results obtained are presented in Table A (at 25 bar) and in Table B (at 15 bar). Whereas one RO-membrane, i.e. only one membrane module (A) does not provide any 18% saccharose solution, a combination of one membrane module (B) and one membrane module (A) provides a production of 0.16-0.17 kg/min/m<sup>2</sup> at 15 bar and a maximum of 0.43 kg/min/m<sup>2</sup> at 25 bar, but a combination of a cascade of two membrane modules (B) with one membrane module (A) provides an increase in production to 0.17-0.21 kg/min/m<sup>2</sup> at 15 bar and to 0.47 kg/min/m<sup>2</sup> at 25 bar.

Table A

|    | Reflux ratio | Production                        |
|----|--------------|-----------------------------------|
|    |              | kg concentrate/min/m <sup>2</sup> |
| 15 | 36           | 0.17                              |
|    | 16           | 0.20                              |
|    | 10           | 0.21                              |
|    | 7.5          | 0.21                              |
| 20 | 6            | 0.20                              |
|    | 0            | 0.00                              |

Though the invention is described for aqueous solutions, other solvents may be used, provided that suitable membranes are selected, in particular organic solvents such as for example benzene, xylene, toluene and pyridine. It will be obvious that the membrane material should be stable with respect to the solvent used.

In the manner described above it is thus possible to compensate for the limitations of RO-membranes by combining membrane modules (A) with high retention membranes (RO-membranes) with membrane modules (B) with limited retention membranes ( $\alpha$ -membranes) said combination providing both higher concentrations and higher productivity than hitherto obtainable.

The invention is further elucidated in the following example

### Example

The example relates to concentrating a 2% aqueous glucose solution to a 20% aqueous glucose solution.

For this purpose were used a cascade of membrane modules (A) with a retention of 99% for glucose, linked in counter-current, and a cascade of membrane modules (B) with a retention of 0.5% for glucose, also linked in counter-current. Additional runs were made with a cascade of membrane modules (A) with one membrane module (B) and another series of runs was made with a combination of one membrane module (A) and a cascade of membrane modules (B). For comparison runs were made with only one membrane module (A) and another series of runs was made with a combination of one membrane module (A) and one membrane module (B). The results of these 15 runs are presented in Table C hereinbelow.

Table C

| Number of modules |     | Production                              |
|-------------------|-----|-----------------------------------------|
| (A)               | (B) | <u>kg concentrate/min/m<sup>2</sup></u> |
| 1                 | 0   | 2.2                                     |
| 20 1              | 1   | 2.7                                     |
| 1                 | 2   | 3.1                                     |
| 2                 | 1   | 3.3                                     |
| 2                 | 2   | 3.8                                     |
| 3                 | 3   | 4.6                                     |

25 From the above data it appears that substantial advantages are obtained by using a combination of membrane modules (A) and (B) with a total number of membrane modules of at least three.

Claims

1. A method for concentrating solutions by means of reverse osmosis, wherein at least one membrane module (A) with high retention for the compound to be concentrated is coupled with at least one membrane module (B) with a limited retention for the compound to be concentrated, the permeate from the (last) membrane module (B) being returned to the (first) membrane module (A), the solvent at the permeate side of the (first) membrane module (A) being removed and the concentrate of the compound to be concentrated being removed at the pressure side of the (first) membrane module (B), while the pressure sides of the (last) membrane module (A) and the (last) membrane module (B) are interconnected, and fresh solution to be treated is supplied at a point in the connection between the permeate side of the (last) membrane module (B) and the pressure side of the (first) membrane module (A), the total number of membrane modules being at least three.
2. Method according to claim 1, characterised in that fresh solution to be treated is supplied at a point upstream from a pump, positioned in the connection between the permeate side of the (last) membrane module (B) and the pressure side of the (first) membrane module (A).
3. A method according to claim 1 or 2, characterised in that a cascade of membrane modules (B) is used.
4. A method according to any one of claims 1, 2 and 3, characterised in that a cascade of membrane modules (A) is used.
5. A method according to any one of claims 3 and 4, characterised in that any cascade comprises from two up to and including eight membrane modules (A) or (B).

6. A method according to any one of the preceding claims, characterised in that at least one of the membrane modules (A) and (B) is a continuous membrane column.

5 7. A method according to any one of claims 3, 4, 5 and 6, characterised in that at least a cascade of membrane modules (B) or a continuous membrane column as membrane module (B) is used, having a separation factor of the membranes used in the direction of the product flow diminishing  
10 from 4 to 1.1.

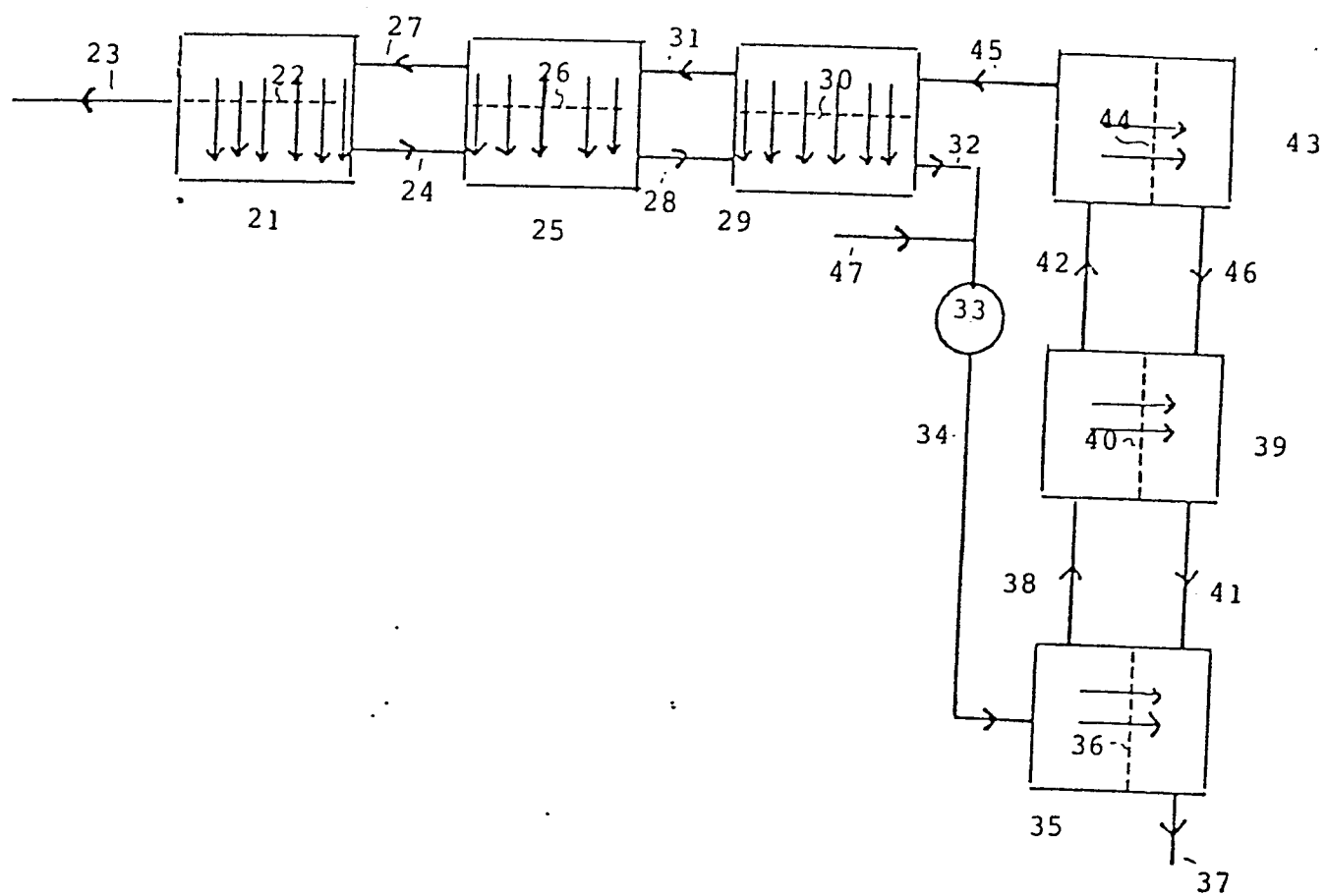
8. An apparatus for concentrating solutions by means of reverse osmosis, comprising at least one membrane module (A) with a high retention for the compound to be concentrated,  
15 ted, coupled with at least one membrane module (B) with limited retention for the compound to be concentrated, the permeate side of the (last) membrane module (B) being connected to the pressure side of the (first) membrane module (A) by a conduit, and the pressure side of the (first) membrane module (A) being connected to the pressure side of  
20 the (last) membrane module (B) by a conduit, the (first) membrane module (A) at the permeate side being provided with an outlet conduit for solvent, the (first) membrane module (B) at the pressure side being provided with an outlet  
25 conduit for formed concentrate, a pump being present in the connecting conduit between the (last) membrane module (B) and the (first) membrane module (A) and at a point between this (last) membrane module (B) and the pump a supply conduit emerging into said connecting conduit, the  
30 total number of membrane modules being at least three.

9. An apparatus according to claim 8, characterised in that it comprises a cascade of membrane modules (B)

35 10. An apparatus according to claim 8 or 9, characterised in that it comprises a cascade of membrane modules (A).

11. An apparatus according to claim 9 or 10, characterised in that any cascade comprises from two up to and including eight membrane modules (A) or (B).
- 5 12. An apparatus according to any one of claims 8-11, characterised in that at least one of the membrane modules (A) and (B) is a continuous membrane column.
- 10 13. An apparatus according to any one of claims 8-12, characterised in that at least one cascade of membrane modules (B) or one continuous membrane column as membrane module (B) has a separation factor of the membranes used in the direction of the product flow diminishing from 4 to 1.1.

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European Patent  
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# EUROPEAN SEARCH REPORT

0070059

Application number

EP 82 20 0800

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                             |                                                |                                                      |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|------------------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Citation of document with indication where appropriate, of relevant passages                                                                                                                                                                | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)       |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | ---<br>US-A-3 617 550 (C.ELATA)<br><br>*Figures; claims 1,2,6,7; column 2, line 12 - column 4, line 52* & GB - A - 1 324 031 (Cat. D)                                                                                                       | 1-6,8-12                                       | B 01 D 13/00                                         |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | ---<br>PATENTS ABSTRACTS OF JAPAN, vol. 3, no. 147, 5th December 1979, page 55 C 66;<br>& JP - A - 54 124 875 (MITSUI TOATSU K.K.K.) (28-09-1979) *Abstract*                                                                                | 1,2,8                                          |                                                      |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | ---<br>US-D- 524 806 (K.K.LADHA)<br>*Figure 1; column 3, line 24 - column 5, line 42; examples I,IV; claims 1,3,6,18,24*                                                                                                                    | 1,2,8                                          |                                                      |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | ---<br>US-A-3 836 457 (M.C.GROSS)<br><br>*Figures 3,4; claims 1,2; column 4, line 21 - column 6, line 23*                                                                                                                                   | 1-6,8-12                                       | TECHNICAL FIELDS SEARCHED (Int. Cl. 3)<br><br>B 01 D |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | ---<br>EP-A-0 029 600 (WERNER UDO)<br><br>*Page 1, line 1 - page 3, line 14; page 6, lines 13-26; page 8, line 8 - page 9, line 18; figures 1,2,5,7; page 16, line 3 - page 17, line 18; page 18, line 18 - page 20, line 9*<br><br>--- -/- | 3-6,9-12                                       |                                                      |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                             |                                                |                                                      |
| Place of search<br>THE HAGUE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                             | Date of completion of the search<br>02-11-1982 | Examiner<br>HOORNAERT P.G.R.J.                       |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document<br><br>T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br><br>& : member of the same patent family, corresponding document |                                                                                                                                                                                                                                             |                                                |                                                      |



| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                          |                                                                               |                                                | Page 2                                         |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|------------------------------------------------|------------------------------------------------|
| Category                                                                                                                                                                                                                                                                     | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3) |
| A                                                                                                                                                                                                                                                                            | GB-A-2 053 024 (DOW CORNING CORP.)<br>*The whole document*                    | 3-6, 9-12                                      |                                                |
|                                                                                                                                                                                                                                                                              |                                                                               |                                                | TECHNICAL FIELDS SEARCHED (Int. Cl. 3)         |
|                                                                                                                                                                                                                                                                              |                                                                               |                                                |                                                |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                   |                                                                               |                                                |                                                |
| Place of search<br>THE HAGUE                                                                                                                                                                                                                                                 |                                                                               | Date of completion of the search<br>02-11-1982 | Examiner<br>HOORNAERT P.G.R.J.                 |
| <b>CATEGORY OF CITED DOCUMENTS</b>                                                                                                                                                                                                                                           |                                                                               |                                                |                                                |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document                                                      |                                                                               |                                                |                                                |
| T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |                                                                               |                                                |                                                |